

# ROLE OF DYNAMIC NUCLEATION AT MOVING BOUNDARIES IN PHASE AND MICROSTRUCTURE SELECTION

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## INTRODUCTION

Solidification microstructures that form under steady-state growth conditions (cells, dendrites, regular eutectics, etc.) are reasonably well understood in comparison to other, more complex microstructures, which form under intrinsically *non-steady-state* growth conditions due to the competition between the nucleation and growth of several phases. Some important practical examples in this latter class include microstructures forming in peritectic systems [1], in highly undercooled droplets [2], and in strip cast stainless steels [3]. Prediction of phase and microstructure selection in these systems has been traditionally based on (i) heterogeneous nucleation on a static interface, and (ii) comparing the relative growth rate of different phase/microstructures under steady-state growth conditions. The formation of new phases, however, occurs via nucleation on, or ahead of, a moving boundary. In addition, the actual selection process is controlled by a complex interaction between the nucleation process and the growth competition between the nuclei and the pre-existing phase under non-steady-state conditions. As a result, it is often difficult to predict which microstructure will form and which phases will be selected under prescribed processing conditions.

This research addresses this critical role of nucleation at moving boundaries in the selection of phases and solidification microstructures through quantitative experiments and numerical modeling in peritectic systems. In order to create a well characterized system in which to study this problem, we focus on the directional solidification of hypo- and hyper-peritectic alloys in the two-phase region, imposing a large enough ratio of temperature gradient/growth rate ( $G/V_p$ ) to suppress the morphological instability of both the parent ( $\alpha$ ) and peritectic ( $\beta$ ) phases, i.e. each phase alone would grow as a planar front. Our combined experimental and theoretical results show that, already in this simplified case, the growth competition of these two phases leads to a rich variety of microstructures that depend sensitively upon the relative importance of nucleation, diffusion, and convection [4, 5, 6, 7].

## GROUND BASED EXPERIMENTS

A set of systematic experiments was carried out to characterize the formation of microstructures in the Sn-Cd. These experiments exploit a new experimental technique developed [4] to directionally solidify several samples simultaneously in capillary tubes with a range of diameters from 0.2 mm to 6 mm, which allows one to systematically reduce and study the effect of convection. The most significant results are the following.

- (1) In the hyperperitectic region, an oscillating structure with seemingly distinct isolated bands was observed. This structure has been widely reported in the literature at large  $G/V_p$  ratio (see [6] and references to earlier work therein). Successive polishing of the samples, however, revealed that this structure is actually made up of two *continuous* interconnected phases in three dimensions. In particular, the microstructure consists of a large tree-like domain of primary  $\alpha$  phase that is embedded inside the peritectic  $\beta$  phase (Fig. 1a). This result is important in that it shows that the widely observed structure is not made up of discrete bands and, hence, is not controlled by nucleation after the first  $\beta$  band is formed.
- (2) This tree-like structure was found to disappear as the sample diameter was reduced, which demonstrates that this structure is the result of the convection present in the bulk liquid. In the hyperperitectic region, only a single  $\alpha$  to  $\beta$  transition is observed (Fig. 1b) in a sample of 0.6 mm diameter where convection is suppressed, as predicted by the diffusive model.
- (3) In the same 0.6 mm diameter sample where convection is suppressed, bands (Fig. 2) that grow by repeated nucleation of the primary and peritectic phases, were observed in a window of composition inside the hypoperitectic region. This result is the first experimental confirmation of the existence of nucleation-controlled *discrete*, as opposed to continuous, band formation in a purely diffusive regime, which had been theoretically predicted but not observed [8].
- (4) The microstructure in the diffusive regime is not unique (Fig. 2) and seems to depend in a complex way on the growth conditions and the nucleation undercoolings of the two phases. In 0.6 mm diameter samples, discrete bands were consistently observed with a large spacing on the order of one mm that is consistent with the prediction of the diffusive model. This spacing, however, was irregular, indicating that the nucleation undercoolings of the two phases can themselves vary in the course of the experiment, most likely due to spatial variations in heterogeneous sites along the sample walls. In 0.4 mm diameter samples, we observed discrete bands that spanned the cross-section either fully or partially leading to the formation of “islands” of the peritectic phase. In addition, coupled growth structures were observed.

## MODELING

Numerical modeling studies were carried out to understand the origin of the different microstructures observed in the convective and diffusive regimes as a function of sample size, composition, and nucleation undercoolings.

A model of convection was developed [5] which shows that the oscillatory microstructures observed in experiments in the hyperperitectic region form due to the presence of oscillating convection in the melt. In this study, the Navier-Stokes equations in the Boussinesq approximation and the heat and solute transport equations are solved numerically inside a two-dimensional rectangular cavity with both horizontal and vertical temperature gradients. These equations are written in a coordinate system that is fixed with respect to the uniformly moving solid-liquid interface. The solid-liquid interface is assumed to remain planar. This assumption renders the computations tractable and makes it possible to capture the main effect of convection on the oscillating microstructures. Numerical calculations were carried out for conditions characteristic of solidification for Sn-1.3 wt% Cd at a growth rate of 3  $\mu\text{m/s}$  in tubes of inner diameter ranging from 0.6 mm to 6.0 mm. The microstructure for a 0.6 mm diameter is diffusion controlled with a sharp transition from  $\alpha$  to  $\beta$  (Fig. 1d). In contrast, for

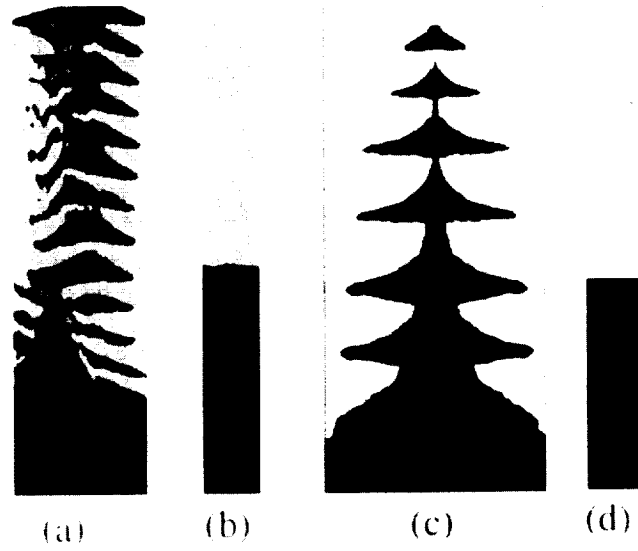


Figure 1: Experimental (a and b) and numerically calculated (c and d) microstructures for a Sn-1.3 wt% Cd alloy for tube diameters  $d = 6$  mm (a and c), and  $d = 0.6$  mm (b and d),  $V_p = 3 \mu\text{m/s}$  and  $G = 13.5$  K/mm.

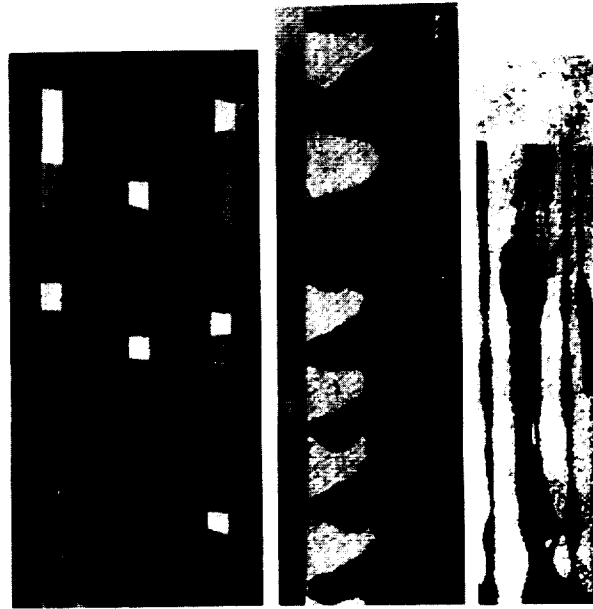


Figure 2: Experimental micrographs showing the variety of possible microstructures in a purely diffusive regime: discrete bands (left,  $d = 0.6$  mm,  $C_0 = 0.9$  wt% Cd,  $V_p = 3 \mu\text{m/s}$ ,  $G = 23$  K/mm), islands (middle,  $d = 1$  mm,  $C_0 = 0.75$  wt% Cd,  $V_p = 4 \mu\text{m/s}$ ,  $G = 23$  K/mm), and coupled growth (right,  $d = 2$  mm,  $C_0 = 0.1.3$  wt% Cd,  $V_p = 1 \mu\text{m/s}$ ,  $G = 13.5$  K/mm).

a 6 mm diameter the convective flow drives an oscillating concentration profile at the interface, which gives rise to an oscillatory coupled growth of the two phases. This oscillatory growth, in turn, generates a tree-like microstructure (Fig. 1c) that is in good qualitative agreement with the experimentally observed one (Fig. 1a).

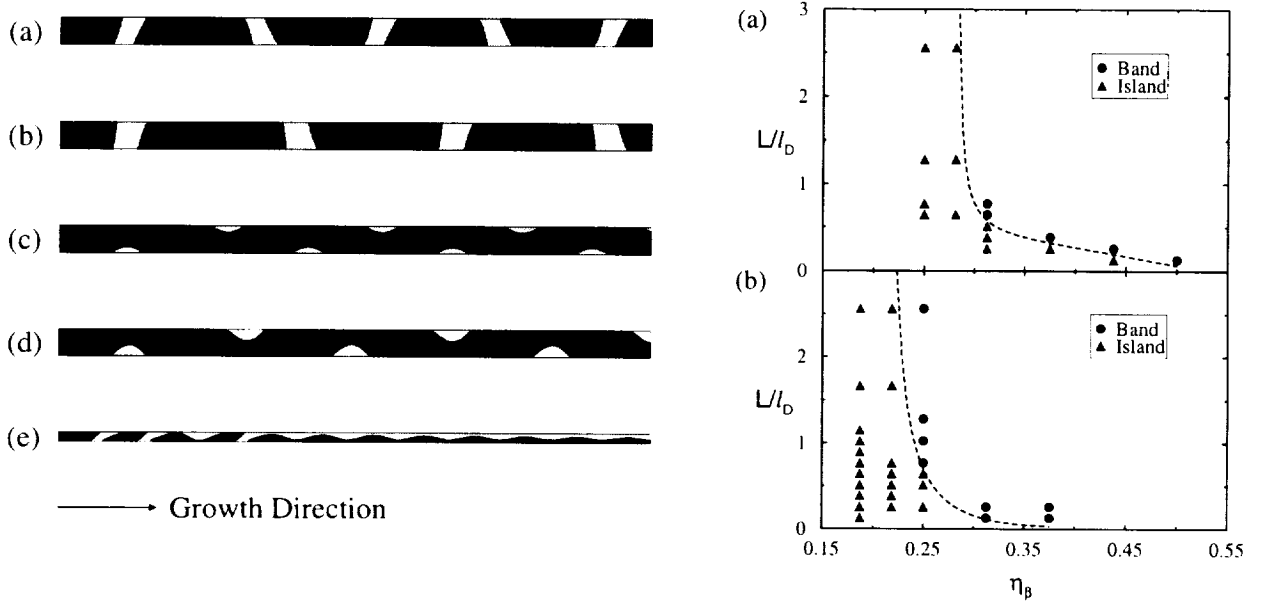


Figure 3: **Left:** Phase-field model simulated microstructures for  $GD/(V|m_\alpha|\Delta C) = 1.116$  and (a)  $\Delta\tilde{T}_N^\alpha = 0.135, \Delta\tilde{T}_N^\beta = 0.0438, L/l_D = 0.512, \eta_\beta = 0.125$ , (b)  $\Delta\tilde{T}_N^\alpha = 0.174, \Delta\tilde{T}_N^\beta = 0.0563, L/l_D = 0.512, \eta_\beta = 0.125$ , (c)  $\Delta\tilde{T}_N^\alpha = 0.0250, L/l_D = 0.512, \eta_\beta = 0.05$ , (d)  $\Delta\tilde{T}_N^\alpha = 0.0312, L/l_D = 0.512, \eta_\beta = 0.075$ , (e)  $\Delta\tilde{T}_N^\alpha = 0.0193, \Delta\tilde{T}_N^\beta = 0.0312, L/l_D = 0.128, \eta_\beta = 0.437$ . **Right:** morphology diagram as a function of system size and volume fraction of the  $\beta$ -phase for two different nucleation undercoolings: (a)  $\Delta\tilde{T}_N^\beta = 0.0312$  and (b)  $\Delta\tilde{T}_N^\beta = 0.0250$ . Here  $\Delta\tilde{T}_N^{\alpha,\beta} \equiv \Delta T_N^{\alpha,\beta}/(|m_\alpha|(C_p - C_\alpha))$  where  $C_\alpha$  and  $C_p$  are the equilibrium composition in  $\alpha$  and liquid phases at the peritectic temperature,  $\eta_\beta$  is the volume fraction of the  $\beta$  phase defined by  $\eta_\beta C_\beta + (1 - \eta_\beta)C_\alpha = C_0$ , and  $l_D = D/V_p$ .

The microstructure in the diffusive regime was investigated by numerical simulation of a fully dynamical phase-field model of peritectic solidification for a generic peritectic phase diagram [7]. The equations of the model were simulated in a rectangular geometry and the microstructure was studied at fixed  $G/V_p$  ratio as a function of the width,  $L$ , of the sample (analogous to the sample diameter  $d$  in the experiments), the composition  $C_0$  inside the hypoperitectic region, measured here in terms of the equilibrium volume fraction of the peritectic phase  $\eta_\beta$ , and the nucleation undercoolings  $\Delta T_N^\alpha$  and  $\Delta T_N^\beta$ .

The simulation results summarized in Fig. 3 show that, below a minimum sample size,  $L_{min}$ , discrete bands of the peritectic phase only fill the sample partially, thereby forming “islands” of this phase, whereas above this minimum they span its entire cross-section. The existence of this minimum size can be understood by noting that partial bands should be formed when the

time for the excess solute rejected by the parent phase to diffuse across the sample is shorter than the time for the peritectic phase to spread across the sample. Since these two times are proportional to  $\sim L^2/D$  and  $L/V_s^\beta$ , respectively, where  $V_s^\beta$  is the lateral spreading velocity of the peritectic phase on the parent phase, equating them yields the estimate  $L_{min} \sim D/V_s^\beta$ .

This estimate contains only one part of the physical mechanism that controls the transition from islands to bands. In particular, our numerical results show that  $L_{min}$  is a function of composition (dashed line in Fig. 3) and becomes infinite at a critical composition, which decreases with increasing nucleation undercooling of the peritectic phase. Below this critical composition  $\beta$  islands form no matter how wide is the sample. The existence of this critical composition can be understood qualitatively by noting that mass conservation implies that the  $\beta$  phase acts as an ‘impurity sink’ that depletes the boundary layer of solute ahead of the growing  $\alpha$ -phase at a rate proportional to  $1 - \eta_\beta$ . Hence, for  $\eta_\beta$  sufficiently small, this sink effect can become large enough to overcome the driving force for the  $\beta$ -phase to spread laterally independently of the sample size.

When the parent phase renucleates on the peritectic phase, it covers it completely only if the sample is smaller than some maximum width  $L_{max}$ . For  $L > L_{max}$ , the parent phase only partially fills the sample and the  $\beta$  phase grows continuously after the first band. In contrast to  $L_{min}$ , which decreases with nucleation undercooling of the peritectic phase,  $L_{max}$  increases with nucleation undercooling of the parent phase. This finding can also be explained semi-quantitatively by comparing the time  $\sim L/V_s^\alpha$  for the  $\alpha$ -phase to spread across the sample to the time  $\sim D/V_p^2$  for the temperature of the  $\alpha$ -liquid interface to fall below the peritectic temperature, which yields the estimate  $L_{max} \sim DV_s^\alpha/V_p^2$ . The fact that  $V_s^\alpha$  increases with  $\Delta T_N^\alpha$  explains our numerical finding that  $L_{max}$  increases with the same quantity.

These results demonstrate that when only a single nucleus is allowed to form on the sample walls, discrete band formation in a diffusive regime is only possible over a finite range of system sizes  $L_{min} < L < L_{max}$  and a finite range of hypoperitectic compositions. Moreover, these ranges depend crucially on the nucleation undercoolings of the two phases. These results also show that other structures than discrete bands can form, which include discrete islands of the  $\beta$  and  $\alpha$  phases for certain ranges of nucleation undercoolings and  $L < L_{min}$  and  $L > L_{max}$ , respectively, as well as more chaotic microstructures.

## NEED FOR MICROGRAVITY AND FUTURE DIRECTIONS

Our results demonstrate unambiguously that convection is playing an especially important role in peritectic systems alloys in comparison to other solidification systems. For example, the basic morphology of cellular, dendritic, or eutectic microstructures is typically influenced quantitatively, but not destroyed, by convection. In contrast, here, convection has a stronger role in that it prevents the formation of nucleation-controlled discrete bands and other more complex microstructures, and leads instead to the continuous growth of oscillating tree-like structures. This is a consequence of the fact that the formation of this class of microstructures is controlled by a delicate competition between growth and nucleation, which is very sensitive to local variations in composition. Thus, future experiments conducted in a microgravity environment will be critically needed to test the microstructural predictions of the diffusive

models in large samples.

The phase-field model results so far agree qualitatively with the experiments in that the microstructure that forms in a diffusive regime depends sensitively on the sample width. A detailed experimental study, however, is now needed to test the model predictions. In addition, the simulations have provided an understanding of the different microstructures that can form in a diffusive regime when only a single nucleus of the new phase is allowed to spread from the walls of the sample. While this restriction is applicable to narrow samples, it is not realistic for wide samples where multiple nuclei can spread simultaneously. Phase-field simulations will be extended to model the formation of microstructures resulting from (i) multiple nucleation events as a function of the composition and the nucleation undercoolings, and (ii) a smaller  $G/V_p$  ratio where one or both phases become morphologically unstable.

For a large  $G/V_p$  ratio, we expect that there should exist a range of nucleation undercoolings where alternate discrete layers of the two phases can form over the entire sample width. In particular, this banded microstructure should form if the mean spacing between  $\beta$ -nuclei is larger than  $L_{min}$ , and the mean spacing between  $\alpha$ -nuclei is smaller than  $L_{max}$ . More complex microstructures that involve the stochastic formation of islands of one phase should be expected to form for other conditions. For a smaller  $G/V_p$  ratio, the simultaneous presence of morphological instability and nucleation of one or both phases should lead to the formation of an even richer class of microstructures that largely remain to be explored.

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